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RADIATION ACTIVATION OF OXYGEN ELECTRODES IN A FUEL CELL

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INTRODUCTION

Present efforts of increasing the activity and capacity of the oxygen electrode in a fuel cell at low and medium temperatures substantially aim at increasing, as much as possible, the contact zones between the gas, the electrolyte, and the electrode (1); and at accelerating the reduction of oxygen to water by catalytically active electrode material or by suitable additives (2). The present paper represents the first portion of an investigation concerning the activation of electrode processes by ionizing radiation, and deals with the influence of β- and γ-emitters, which are deposited on the electrode, upon the oxygen electrode and its capacity.

It is known that the yield in homogeneous processes, which have been activated by radiation chemistry, is low in respect to the radiation energy absorbed (G values in the order of magnitude of 0.5-5), in the absence of a chain mechanism. A number of investigations have been conducted on the other hand, wherein it was shown that heterogeneous catalytic reactions are accelerated by ionizing radiation. Permanent increases in activation have been achieved particularly by radiation in semiconductor catalysts, although these results are not entirely without contradiction (3). V. I. Spizyn et al (4) were able to find noteworthy activation increases with catalysts, when the catalyst itself is rendered radioactive, evidently because this substantially increases the absorbed dosage of rays, and the catalyst structure is changed.

EXPERIMENTAL PROCEDURE

Our experiments, up to this time, dealt with the addition of β- and γ-emitters to the electrode, which was contacted with 0_2. No clear effect, so far, has been shown by orientation measurements concerning the influence of external X-ray radiation upon the velocity of achieving the oxygen potential and its change during load; so that they shall not be discussed here. The preliminary electrode material was platinum or nickel in the form of sheets, sieves, or cylinders, on which the radioactive elements Ru 106, Ir 192, Tl 204, and Po 210 were precipitated electrolytically. The element was coated with platinum if a risk existed that the element would participate directly in the electrode process, such as in the case of Tl 204 and Po 210. The radiation source was situated in a platinum capsule, when a dense, solid isolation was not possible. The capsule was introduced into the cylindrical electrode of platinum wire mesh. The distance between the radiation source and the electrode was about 0.5 mm, and the interspace was filled with gaseous 0_2 during the measurement. Accordingly, it is not a question here of a direct activation of the electrode, but of radiation (see below). Table 1 shows the radionuclei used so far, showing their half life, decomposition process, energies of the emitted particles and the γ-radiation, as well as the distribution of the radiation energy in question. The Pt-, Ir-, and Au-isotopes were produced by irradiating inactive electrodes in a reactor.

The electrolyte generally was 1 m KOH. The measurements were performed in a cell as shown in Figure 1, and the greatest emphasis was placed upon comparable experimental conditions. A constant current was imparted to the oxygen electrode during capacity measurements, with the aid of an external voltage source of 100 volts and a suitably high resistance. Its potential change as a function of time was measured against a reference saturated calomel electrode.

Table 1

Isotope	Half Life	Type of Decomposition	Particle	% Frequency	Quant. MeV	% Distribution
P-32	14, 3 d	β^- (100%)	1.701	100	-	-
Ru-106	1, 0 a	β^- (100%)	0.0392	100	-	-
Rh-106	30 sec.	β^- (100%)	3.53	68	0.513	11
			3.1	11	0.624	5.8
			2.44	12	0.87	0.3
					1.045	0.9
			2.0	3	1.55	0.3
					2.41	0.1
Ir-192	74, 37 d	β^- (95,5%)	0.675	48	0.201	0.4
		β^- (10^{-4}%)	0.535	41	0.206	3.5
			0.257	7	0.283	0.5
		K (4, 5%)	0.100	< 0.5	0.295	32
					0.308	31
					0.316	89
					0.375	1.7
					0.416	1.4
					0.468	57
					0.485	3.5
					0.588	6.3
					0.604	12.5
					0.613	7.5
					0.885	0.4
Pt-193^m	4, 33 d	K (100%)	-		0.135	
		Isom. (100%)			0.2	
					1.5	
Pt-195^m	3.5 d	K (100%)	-		0.029	
					0.097	
					0.126	
					0.129	
Pt-197	18 h	β^- (100%)	0.670	88.5	0.077	99
			0.479	10.6	0.191	10.6
			0.468	0.9	0.279	0.9
Au-199	3.15 d	β^- (100%)	0.460	4	0.050	3.5
			0.297	73	0.159	77
			0.250	23	0.209	19
Tl-204	4.02 a	($\sim$ 97%)	0.766	$\sim$ 97	0.380	3
	2.50 a	K ($\sim$ 3%)				
Po-210	138.4 d	α (100%)	5.298	100	0.803	10^{-3}
			4.511	$\sim 10^{-3}$		

RESULTS

Only orientation tests have been performed with the radiation sources of Table 1 at this time. Accordingly, this report will deal only with the results achieved with Tl 204 and with Ru 106, especially since these two radiation nuclei probably deserve the most practical interest, owing to their relatively great half life.

It was examined first whether the radiation source has an influence upon the velocity, with which a stationary oxygen potential is established. Figure 2 represents the potential time curve of 5 platinized platinum electrodes, which were contacted with oxygen. It can be seen that the electrodes behave differently, but that a stationary end value is achieved after about 20 minutes. This end value is 200-250 mV below the reversible value. Figure 3 shows the potential time curves for 4 electrodes, which are completely identical with those in Figure 2, after about 3 mC Tl 204/cm^2 had been deposited upon them, and they had been coated again with Pt. These electrodes show a more uniform behavior, establish a stationary value in about 10 minutes, and this value is only about 150-180 mV below the reversible oxygen potential. Figure 4 shows the potential course of these electrodes with an increase in load; the dotted line represents the average course of the electrodes, which were activated with Tl 204, while the full curve shows the average course of the platinized platinum electrodes. It can be seen clearly that the radiation of Tl 204 produces a higher stability of the stationary potential during load, in spite of considerable dispersion. These results were checked by measurements at constant current and the potential course was monitored. Figures 5 and 6 show that the electrodes, which have not been activated, show a more irregular behavior and a faster potential drop (Figure 5) than the activated electrodes (Figure 6), where the potential course is uniform, corresponding to the load and, particularly at 3 ma/cm^2, is much less.

Constant current measurements likewise were performed for Pt electrodes, on which various quantities of Ru 106 had been deposited, and which then again had been platinized. These measurements are represented in Figure 7. The curves designated as No. 1 relate to inactive electrodes, while those designated as No. 2 relate to electrodes, which were activated with 110 mC Ru 106/cm^2. Although activity per cm^2 is substantially greater than the Tl 204, the effect regarding the stabilization of the potential during load is not so clear. Measurements with electrodes, which contained 28 mC/cm^2 of Ru 106, showed approximately the same behavior.

In additional experiments, 45 mC of Ru 106 were placed in a capsule, which was separate from the electrodes, so that it was possible to investigate the same electrode with and without the β-radiation effect of Ru 106. Figure 8 shows that the potential drop of the irradiated electrode during load is not quite so steep as without irradiation, but the difference is slight and requires checking under constant current conditions. The orientation measurements with electrodes, which contained other radionuclei, showed substantially the same differences in comparison with inactive electrodes.

DISCUSSION

Present measurements show that the action of ionizing radiation upon the oxygen electrode accelerates the approach to the stationary potential and the potential value reached is closer to the reversible potential, if the radiation source is situated on the electrode itself. Accordingly, a lower potential drop also occurs during load. It can be assumed, therefore, that the radiation effect accelerates the reduction of 0_2 to H_20_2 or H_20 at the electrode surface. No definite statements can be made now concerning the mechanism of this effect, but it definitely is not probable that the β- or γ-energy influences directly the activation process. Rather, it must be assumed that it increases the activity of the electrode surface and thereby facilitates the reduction process. The present results show that Tl 204 has a greater effect than Ru 106 at a lower level of radioactivity per cm^2; this can be because of its greater β-energy. This, however, requires a thorough investigation, as our measurements in general represent only a beginning. Present tests concern particularly an investigation of the activation of coals by radionuclei.

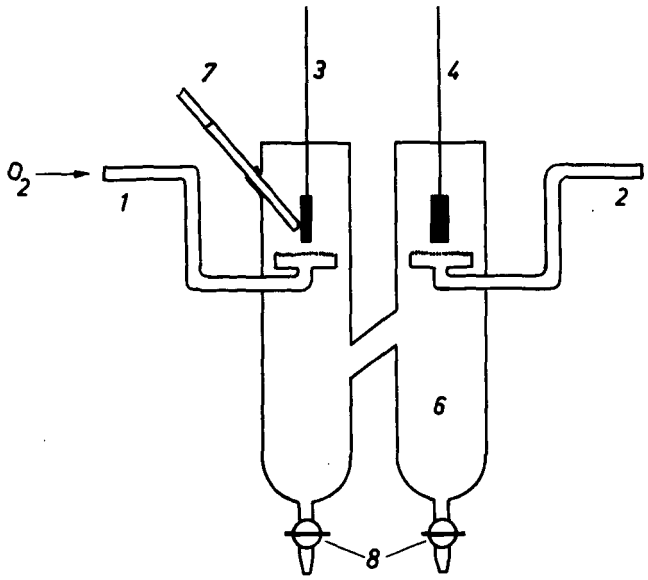

FIGURE 1

1. O_2-Einleitung
2. H_2-Einleitung
3. Kathode
4. Anode
5. Diaphragma
6. Elektrolyt
7. zur Bezugselektrode
8. Hähne zur Entnahme des Elektrolyten

FIGURE 2

Potential-Zeit-Diagramme von unbelasteten inaktiven Elektroden in 1 n KOH
reversibles O_2-Potential + 0,16 V

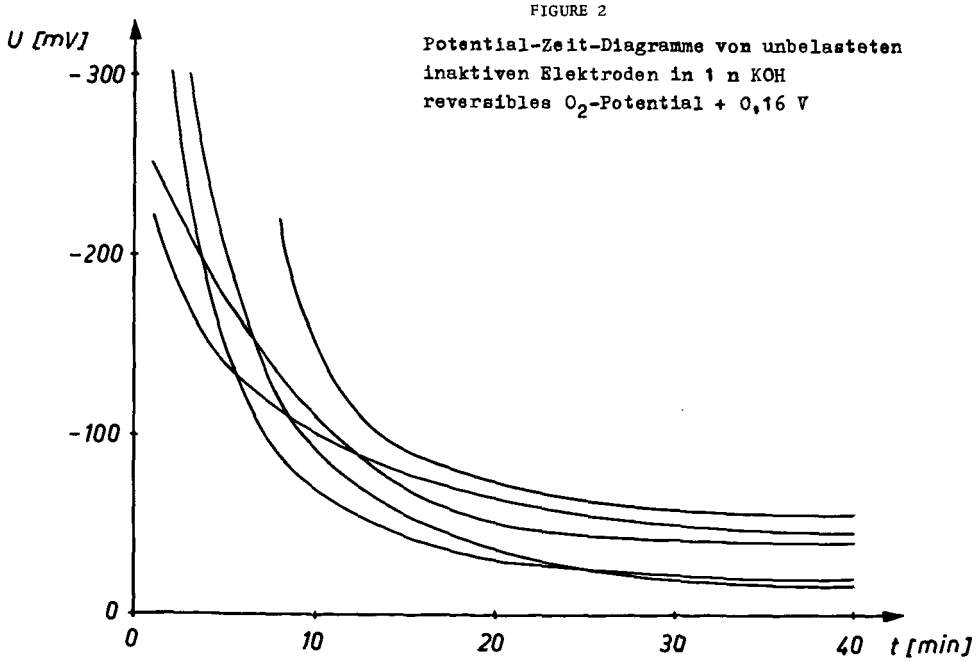

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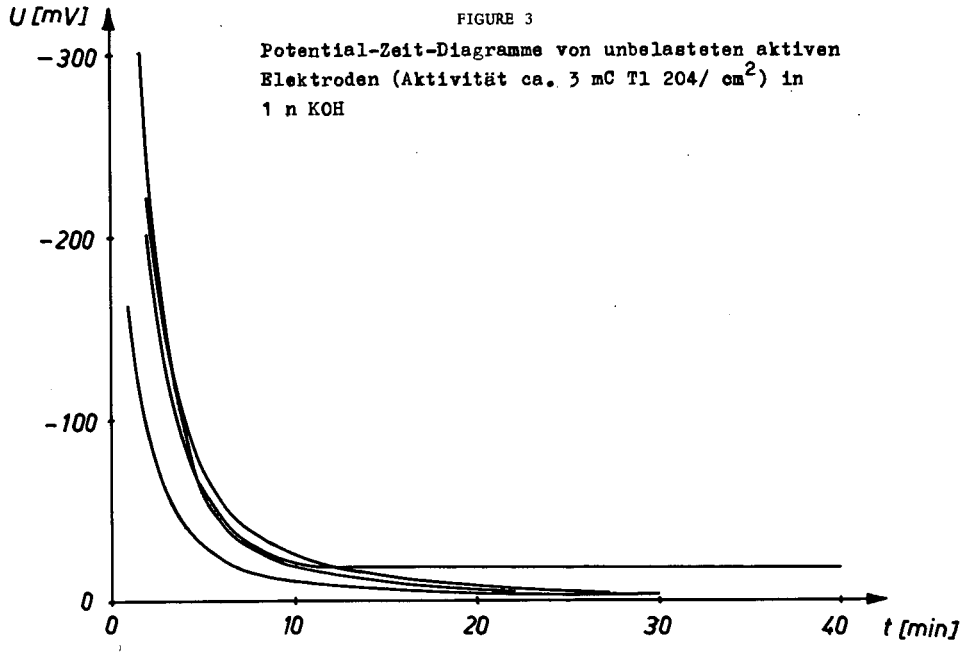
FIGURE 3

Potential-Zeit-Diagramme von unbelasteten aktiven Elektroden (Aktivität ca. 3 mC Tl 204/ cm^2) in 1 n KOH



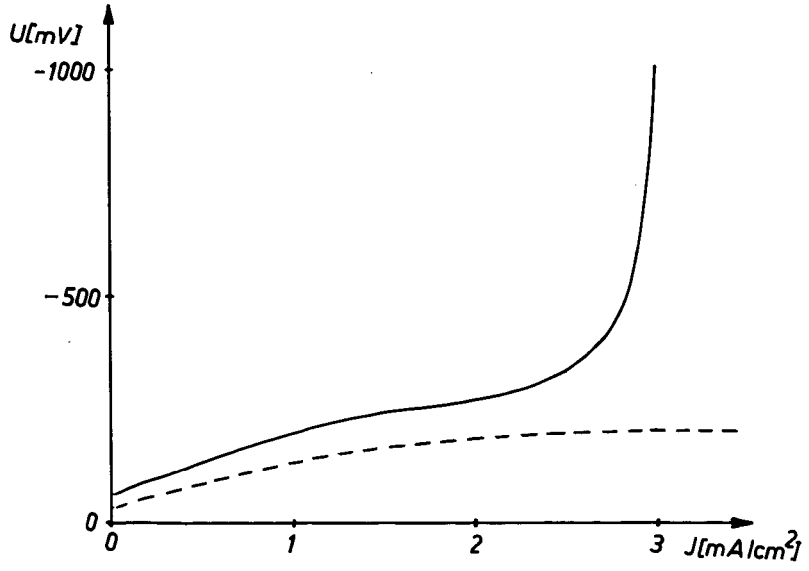


FIGURE 4

Potential-Stromdichte-Diagramme aktiver —— (Tl 204) und inaktiver ___ Elektroden. (Mittelwerte aus 5 Meßreihen)

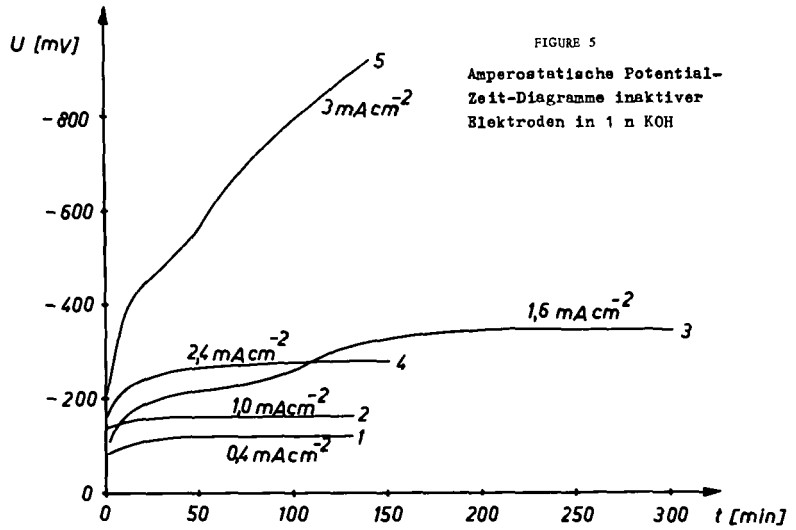


FIGURE 5

Amperostatische Potential-Zeit-Diagramme inaktiver Elektroden in 1 n KOH

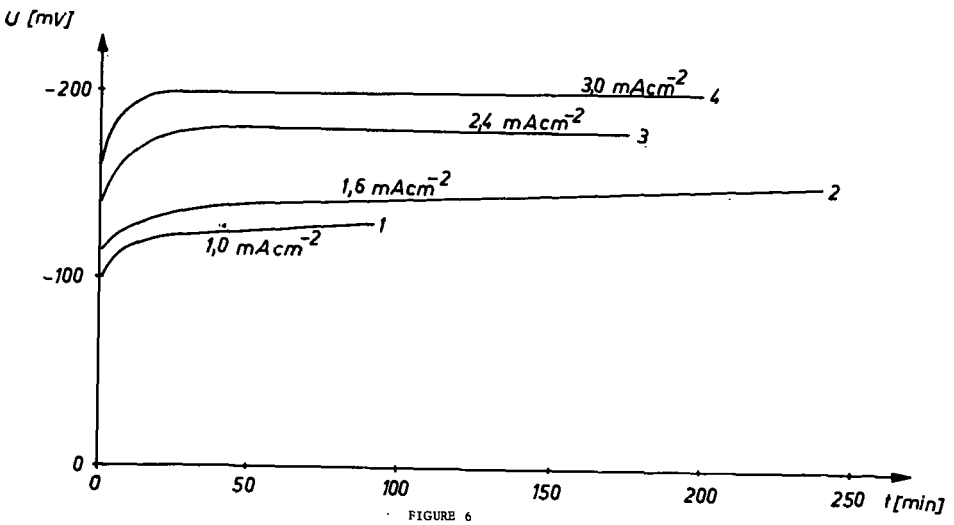


FIGURE 6

Amperostatische Potential-Zeit-Diagramme aktiver Elektroden in 1 n KOH, Aktivität der Elektroden 3 mC Tl 204/ cm^2

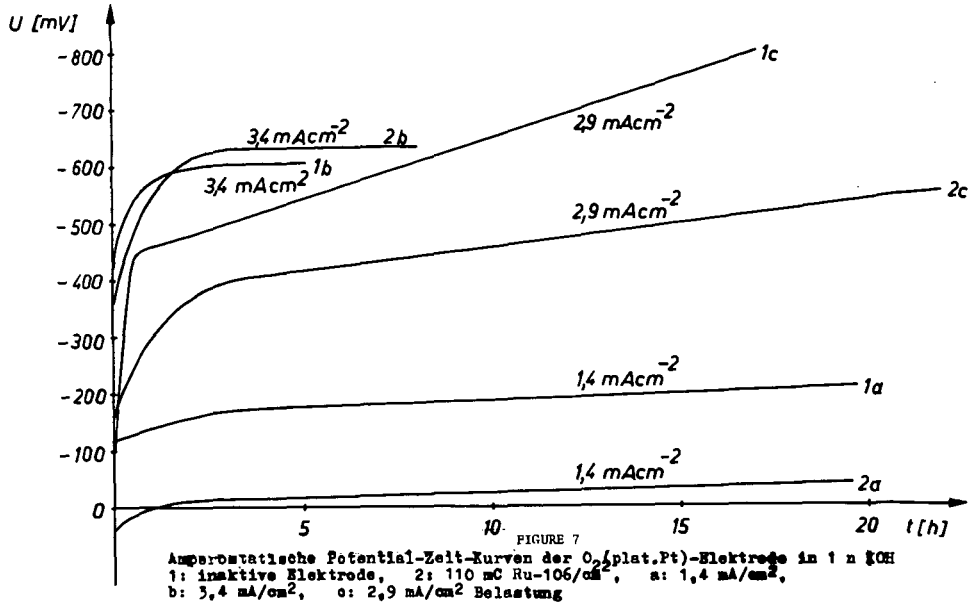


FIGURE 7

Amperostatische Potential-Zeit-Kurven der O_2(plat.Pt)-Elektrode in 1 n KOH
1: inaktive Elektrode, 2: 110 mC Ru-106/cm², a: 1,4 mA/cm²,
b: 3,4 mA/cm², c: 2,9 mA/cm² Belastung

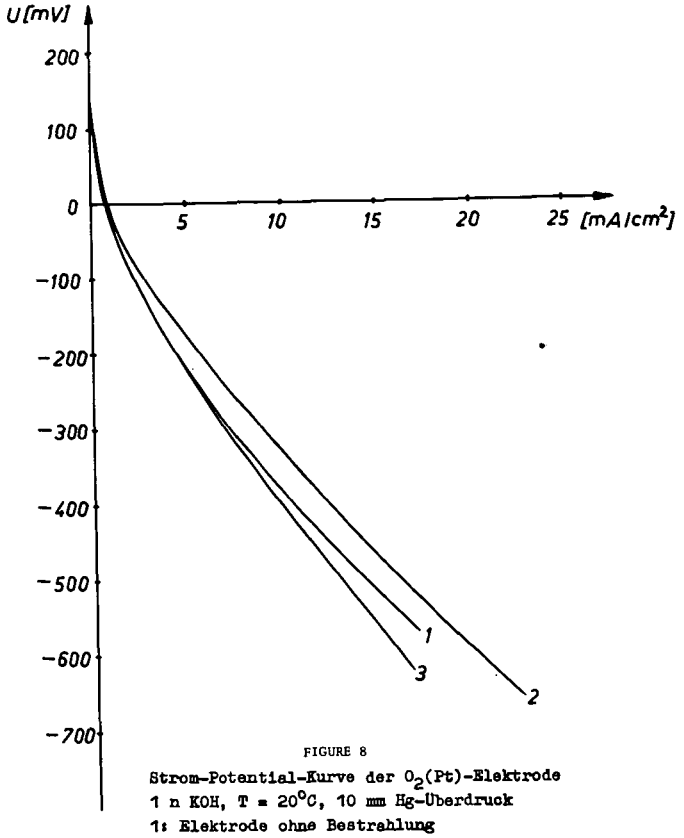


FIGURE 8

Strom-Potential-Kurve der O_2(Pt)-Elektrode
1 n KOH, T = 20°C, 10 mm Hg-Überdruck
1: Elektrode ohne Bestrahlung
2: Elektrode mit 45 mC Ru-106 bestrahlt
3: Elektrode nach Entfernung der Strahlenquelle